

Intermolecular Potentials for the H₂O-C₆H₆ and the C₆H₆-C₆H₆ Systems Calculated in an ab Initio SCF CI Approximation

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Abstract: Ab initio SCF CI potentials have been calculated for the H₂O-C₆H₆ and the C₆H₆-C₆H₆ systems. The interaction energy is decomposed into contributions that could be given a physical interpretation. It is shown that it is necessary to obtain good estimates for each of these contributions in order to obtain a reliable potential. The calculated potentials are fitted to analytical forms, and the second virial coefficient for the C₆H₆-C₆H₆ system as well as the cross virial coefficient for the C₆H₆-H₂O system is calculated.

Introduction

Monte Carlo and molecular dynamics simulations have turned out to be a valuable tool in the study of condensed matter. Starting with a knowledge of the molecular interactions, the simulation techniques provide means for obtaining thermodynamic as well as transport properties of the liquid and solid states. A number of simulations of pure liquids and aqueous solutions have been performed during the last few years. In the simulation of aqueous solutions of nonpolar solutes, a special interest has been directed toward an understanding and description of the so-called hydrophobic effect.^{1,2} Experimentally, it is found that the process of dissolving a small hydrocarbon molecule in water is entropically controlled at room temperature,³ and indeed, simulations of methane in water indicate an ordered water structure around the methane molecule.⁴⁻⁶ On the other hand, it is well-known that the free-energy interaction between a hydrocarbon phase and a water phase is largely determined by the enthalpic term.⁷ The benzene molecule falls somewhere in between, in that the entropic and enthalpic terms work in the same direction and hence give a low solubility of benzene in water.⁸ It is also experimentally well-known that the solubility of water in benzene is small, but the structural effects of a water molecule in benzene are not accessible by experimental techniques. Considering these facts, it seems that a Monte Carlo (MC) or a molecular dynamics (MD) simulation of benzene in water and water in benzene may increase our understanding of the interaction between water and nonpolar molecules and of the hydrophobic effect. However, in order to make such a simulation meaningful, it is necessary to have good intermolecular potentials between water and benzene as well as between benzene and benzene. The water-water interaction potential is already available in the literature in a number of approximations.⁹⁻²¹

One obvious way to obtain intermolecular potentials is to use quantum chemical methods and solve the Schrödinger equation for the interacting molecules in some suitable approximation. This approach has been used by several groups^{5,13-18} pioneered by Clementi and co-workers.⁹ Another possibility is to use experimental data to parametrize a function describing the interaction. The ST2 potential for water is a well-known result of this approach.¹² A third possibility, which has only been used occasionally, is to combine theoretical and experimental information and construct a semiempirical intermolecular potential. In this communication, we will focus on the first alternative, the non-empirical intermolecular potential.

The well-known H₂O-H₂O potential of Matsouka, Clementi, and Yoshimine (MCY potential)⁹ was obtained from ab initio calculations using an extended basis set, and the dispersion energy was calculated by a configuration interaction (CI) procedure. This is still impossible to do for larger polyatomic molecules, and only

a few intermolecular potentials of comparable accuracy, in addition to those dealing with rare-gas atoms, have been published.^{15,17-18} Most work done so far has been restricted to small- and medium-sized basis sets and then primarily within the Hartree-Fock approximation. In the rare cases with larger basis sets, where a calculation of the dispersion energy is meaningful, it has usually been done via a London-type dispersion calculation.¹⁹

However, as pointed out some time ago,²⁰ and recently emphasized by several workers,^{14,18} the use of limited basis sets may lead to an artificial stabilization of the interacting molecules. This so-called basis set superposition error (BSSE) can be approximately corrected for by using the counterpoise method.²⁰ Recently, it has been shown that there exists a "second-order" BSSE that affects the multipole moments and polarizability of the monomers and that cannot be handled by the counterpoise technique. Fortunately, this seems to be an order of magnitude smaller and can thus be neglected in most cases.²¹

The calculation of intermolecular potentials thus puts rather severe restrictions on the basis sets: they must reproduce the monomer properties including the molecular polarizability, and they must not give rise to a large BSSE. Very few, if any, basis sets fulfill these requirements. For example, the minimum energy for the (HF)₂ dimer has been calculated by using a very large basis set by Lischka²² to be -3.8 kcal/mol as compared to the

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STO-6-31G value of -8 kcal/mol.¹³

Summarizing these facts, there appears to be a need for a consistent procedure for calculating intermolecular potentials between polyatomic molecules. In the next section, we will attempt to derive such a procedure. It is based on the observation that the exchange repulsion term is well described even with a minimal basis set.²³ The electrostatic, induction, and dispersion interaction can then be estimated with larger basis sets without having to perform a full SCF CI calculation for every dimer geometry. The presented model is then used to calculate intermolecular potentials for the water-benzene and the benzene-benzene systems. These potentials are used to calculate second virial coefficients and are compared with experimental data.

Computational Strategy

The total SCF interaction energy may be partitioned into different, more or less physical, terms:²⁴

$$\Delta E_{\text{SCF}} = E_{\text{es}} + E_{\text{ind}} + E_{\text{ex}} + E_{\text{ci}} + E_{\text{mix}} \quad (1)$$

where E_{es} is the electrostatic interaction, E_{ex} the exchange repulsion, E_{ind} the electrostatic induction term, E_{ci} the charge-transfer energy, and E_{mix} contains coupling terms. In an earlier work, it was shown that when ΔE_{SCF} was corrected for the basis set superposition error, E_{BSSE} , the sum of all terms directly related to the electronic overlap was fairly constant for a number of basis sets of varying size²³ (the term most affected by E_{BSSE} was the charge-transfer term). Thus we may write

$$\Delta E_{\text{SCF}}^{\text{corr}} = E_{\text{es}} + E_{\text{ind}} + (E_{\text{ex}} + E_{\text{ci}} + E_{\text{mix}} + E_{\text{BSSE}}) \quad (2)$$

where the sum in parenthesis is to a considerable degree independent of the basis set. The term E_{BSSE} is defined as

$$E_{\text{BSSE}} = E_{\text{A}}(\text{A}) + E_{\text{B}}(\text{B}) - E_{\text{A}}(\text{AB}) - E_{\text{B}}(\text{AB}) \quad (3)$$

where $E_{\text{A}}(\text{A})$ is the energy for monomer A calculated with the basis functions of A, and $E_{\text{A}}(\text{AB})$ is the monomer energy calculated including also the basis functions of monomer B. An analogous interpretation holds for $E_{\text{B}}(\text{B})$ and $E_{\text{B}}(\text{AB})$. Thus, if it were possible to calculate the electrostatic and induction terms for a large basis set without performing an explicit SCF calculation on the dimer, then one could obtain an accurate estimate of $\Delta E_{\text{SCF}}^{\text{corr}}$ by correcting a minimal basis calculation for the difference in $E_{\text{es}} + E_{\text{ind}}$ estimated with the large and small basis, respectively. The approximate interaction energy would then read

$$\Delta E_{\text{SCF}} \approx \Delta E_{\text{SCF}}^* + E_{\text{BSSE}}^* + (E_{\text{es}} - E_{\text{es}}^*) + (E_{\text{ind}} - E_{\text{ind}}^*) \quad (4)$$

where an asterisk indicates a small basis quantity.

Electrostatic and Induction Energies. The exact evaluation of the electrostatic interaction between two molecules, A and B, is given by

$$E_{\text{es}} = \int \rho_{\text{A}}(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \rho_{\text{B}}(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (5)$$

where $\rho_{\text{A,B}}$ are the molecular charge distributions. To evaluate such an expression, it is necessary to compute all two-electron integrals of type $\langle \chi_i(1)\chi_j(1)(1/|r_{12}|\chi_k(2)\chi_l(2)) \rangle$, which is too time consuming with a large basis set. An alternative is to expand ρ in a *multicenter* multipole expansion and to evaluate E_{es} in eq 5 as the interaction between two such expansions. This can be done for the small basis so as to obtain E_{es}^* and also for almost any large basis set and hence gives the difference $E_{\text{es}} - E_{\text{es}}^*$ in eq 4.

The electronic part of the molecular charge distribution, ρ , may be expanded as

$$\rho = \sum_{ij} D_{ij} \chi_i \chi_j \quad (6)$$

where D_{ij} is a density matrix element and χ_i a basis function

Table I. Dispersion Energy for the H₂O-C₆H₆ System Calculated with Three Different Methods^a

| <i>R</i> , Å | dispersion energy, kcal/mol | | |
|--------------|-----------------------------|----------------|---------------------------|
| | CI | Møller-Plesset | multipole exptl (eq 8) |
| 3.70 | 0.15 | 0.16 | 0.15 |
| 4.23 | 0.10 | 0.09 | 0.08 |
| 5.29 | 0.04 | 0.04 | 0.04 |

^a The distance between the benzene center of mass and the water oxygen is represented by *R*. The two symmetry axes coincide, and the water oxygen is pointing toward the benzene molecule.

centered on a nucleus. This means that each element D_{ij} may be assigned to a pair of nuclei and thus the total density ρ may be split up into local contributions according to

$$\rho_{\text{KL}} = \sum_{i \in \text{K}} \sum_{j \in \text{L}} E_{ij} \chi_i \chi_j \quad (7)$$

where K and L stand for the nuclei. With this partitioning of the total density, each contribution ρ_{KL} has a rather limited extension in space, and a multipole expansion of ρ_{KL} could be expected to converge rapidly. In the present work, the multicenter multipole expansions are truncated after the quadrupole terms. As a consequence, the total electrostatic energy between the two molecules will include all terms up to quadrupole-quadrupole interactions. This is consistent for the interaction between H₂O and C₆H₆, as well as for the C₆H₆ dimer, since the benzene molecule has no dipole or octupole moment.

In a recent work, a method was presented²⁵ for partitioning the total molecular polarizability into local contributions based on ab initio HF calculations. The partitioning is based on the observation that the total polarizability (in the uncoupled Hartree-Fock approximation) may be split up into four index contributions, where two indices refer to basis functions in occupied orbitals and two to basis functions in virtual orbitals. By summing over the virtual orbitals, a set of pseudo-two-index contributions may be obtained. Given these local polarizabilities and a multicenter multipole expansion of the charge distribution, the calculation of the induction energy is straightforward. The correction for the errors in the induction term has only been performed for the water-benzene system since only terms of dipole-induced dipole type are considered.

Dispersion Energy. Recently, a method for the evaluation of the dispersion interaction was published.²⁵ The method is based on a second-order estimate of the dispersion term:

$$E_{\text{disp}} = 4 \sum_{ij} \sum_{kl} \frac{|\langle \phi_i(1)\phi_j(1)(1/r_{12})\phi_k(2)\phi_l(2) \rangle|^2}{\epsilon_i - \epsilon_j + \epsilon_k - \epsilon_l} \quad (8)$$

where ϕ_i and ϕ_k are occupied orbitals and ϕ_j and ϕ_l virtual orbitals on the two molecules, respectively. The denominator contains the corresponding orbital energies. In the method proposed, it is assumed that the charge distributions $\phi_i(1)\phi_j(1)$ and $\phi_k(2)\phi_l(2)$ do not overlap, so that they can be described by a multipole expansion. The interaction energy E_{disp} is then approximated to include only the dipole-dipole and dipole-quadrupole terms.

Since the canonical benzene orbitals have a large extension in space, the multipole expansion of $\phi_i(1)\phi_j(1)$ may be slowly convergent. This problem can, however, be avoided by localizing the canonical orbitals. In the localization procedure,²⁷ the orbitals have been divided into different groups with similar orbital energies. The localization has then been performed within each group in order to avoid mixing of orbitals with large differences in their orbital energies.

In order to indicate the accuracy of the above described procedure, the dispersion energy has been calculated with a minimal

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Table II. Calculated (Extended Basis Set) and Experimental Multipole Moments and Polarizability Tensor for Water and Benzene^a (Atomic Units Are Used)

| | H ₂ O | | C ₆ H ₆ | |
|----------------------------|------------------|-------------------|-------------------------------|-------------------|
| | calcd | exptl | calcd | exptl |
| μ | 0.78 | 0.73 ^d | | |
| θ_{xx} | 1.90 | 1.96 ^e | 3.40 | 3.7 ^g |
| θ_{yy} | -1.87 | -1.86 | 3.40 | 3.7 ^g |
| θ_{zz} | -0.03 | -0.10 | -6.80 | -7.4 ^g |
| α_{xx} | 7.3 | | 71.9 | |
| α_{yy} | 8.6 | | 71.9 | |
| α_{zz} | 7.7 | | 42.1 | |
| α_{tr} ^c | 7.9 | 9.7 ^f | 62.0 | 64.9 ^h |

^a The geometries used in the calculations were $r_{OH} = 0.946$ Å, $\angle HOH = 106.35^\circ$, $r_{CC} = 1.395$ Å, and $r_{CH} = 1.084$ Å. ^b Symmetry axis. ^c $\alpha_{tr} = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. ^d Reference 37. ^e Verhoeven, J.; Dymannus, A. *J. Chem. Phys.* 1970, 52, 3222. ^f Comprehensive Inorganic Chemistry; Pergamon Press: New York, 1973; Vol. 1-2. ^g Reference 38. ^h Atkins, P. W. "Physical Chemistry"; Oxford Press: Oxford, 1978.

basis set using three different approximations, and the result is shown in Table I. The first method in Table I is a standard CI calculation including all single and double replacements out of the Hartree-Fock reference state, the second estimate is based on a second-order Møller-Plesset calculation,²⁸ and the third method is based on a multipole expansion of eq 8 using localized orbitals. Table I shows that the multipole expansion reproduces the CI and Møller-Plesset values fairly well, and since other systems have been tested²⁶ and found to behave similarly, we feel rather confident that the proposed method is able to reproduce *small basis set* estimates of the dispersion energy. The extension of the method to large basis sets is nontrivial and is discussed in Appendix 1.

Quantum Mechanical Calculations and Their Results

Following the method described above, we have calculated intermolecular potentials for the water-benzene and benzene-benzene systems. The minimal basis set used consisted of 7 s and 3 p primitive functions on oxygen and carbon contracted to 2 s and 1 p, respectively.²⁹ The hydrogen primitive basis consisted of 3 s contracted to one single function.³⁰ The large basis calculations were performed with a (9 s, 5 p) primitive basis set contracted to (5 s, 3 p) for O and to (4 s, 2 p) for C.³¹ The oxygen basis set was then augmented with one diffuse s and one diffuse p function as well as one valence and one diffuse d function. The carbon basis set was augmented in the same way as the oxygen basis set, but no diffuse d function was added. The hydrogen basis set in water was constructed from (5 s) primitives contracted to (3 s)³⁰ to which one diffuse s function and one valence p and one diffuse p function had been added. The hydrogen basis set in the benzene molecule was constructed from (5 s) contracted to (2 s)³⁰ and augmented with one valence p orbital.

Each point on the intermolecular surface took ~ 35 (H₂O-C₆H₆) and 140 min (C₆H₆-C₆H₆), respectively, of computer time on a Univac 1100/80 including the correction of the electrostatic and induction energies and the dispersion energy calculation. The monomer geometries were held fixed, and they are presented in Table II together with experimental and calculated monomer properties. The agreement between experimental results and the extended basis set values is reasonable and may at most give rise to an error of 10-15% of electrostatic interaction in the intermolecular potential.

The total interaction energy is the sum of the corrected SCF energy and the dispersion energy (eq 4 and 8):

$$\Delta E_{\text{tot}} = \Delta E_{\text{SCF}} + E_{\text{disp}} \quad (9)$$

(28) The Møller-Plesset energy is obtained in a second-order perturbation calculation where orbital energies are used in the denominator.

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Table III shows the importance of the different contributions to ΔE_{tot} as a function of intermolecular separation for two different water-benzene orientations. The values in Table III clearly show that a straightforward calculation with a minimal basis set can *at best* give a qualitative picture of the true intermolecular potential. It can also be seen that for orientation I, $-E_{\text{disp}} \gg E_{\text{BSSE}}$, while for orientation II, $-E_{\text{disp}} \approx E_{\text{BSSE}}$ near the minimum. Thus, the two terms do not in general cancel, which seems to be the underlying assumption in these minimal basis calculations, where the BSSE and the dispersion energy are neglected.¹⁰ These conclusions are also strongly supported by a similar analysis of the benzene-benzene interaction energies. The first and close to the most stable orientation for the water-benzene system is one where the symmetry axes of the two molecules coincide and the water hydrogens point toward the benzene molecule. This structure is analogous to the minimum in the HCl-C₆H₆ complex found by Nelander³² using matrix isolation techniques and by Read et al.³³ using microwave spectroscopy. It is interesting to note that this geometry is favored by the electrostatic and the exchange repulsion energy. The second orientation is one where the two molecules lie in the same plane and the water symmetry axis coincides with one C₂ axis of benzene going through two hydrogen atoms (see also Figure 1 for the relative orientations). The benzene dimer is a more studied system, and in a recent work,³⁴ Steed et al. showed that the dimer has a dipole moment and concluded that the dimer consists of two perpendicular benzene molecules, which is also supported by our results (see Figure 3).

Construction of Analytic Potentials

The calculated points on the two intermolecular energy surfaces were fitted, by using a least-squares procedure, to functions of the following form:

$$E_n = \sum_i \left[A_i \frac{1}{r_{in}} + B_i \frac{1}{r_{in}^4} + C_i \frac{1}{r_{in}^6} + D_i \frac{1}{r_{in}^9} + E_i \frac{1}{r_{in}^{12}} \right] \quad (10)$$

where i sums over the interatomic distances C-O, C-H(water), H(benzene)-O, and H(benzene)-H(water) in the H₂O-C₆H₆ case, and similarly over the C-C, C-H, and H-H distances in the benzene dimer. The coefficients A_i were chosen to reproduce experimental dipole and quadrupole moments.^{34,35} In order to obtain correct long-range r dependence, the coefficients B_i were chosen to be linearly dependent. The coefficients E_i were calculated from van der Waals data and not fitted. The fit was done in an iterative way by successively extending the number of calculated points. The predictive capability of the actual potential function was tested after the calculation of each batch of new points. The coefficients of the potential functions are given in Tables IV and V. In the fitting procedure, a weighting function

$$w_n = \exp(-E_n/RT) \quad T = 300 \text{ K} \quad (11)$$

was used for repulsive points, and the least-squares sum was defined as

$$\epsilon^2 = \sum_n (E_n^{\text{calcd}} - E_n^{\text{fit}})^2 w_n / \sum_n w_n \quad (12)$$

The water-benzene potential function was based on 153 points, and a value of 0.24 kcal/mol was obtained for ϵ in the fit. Figure 1 shows the potential energy curve produced by the function together with calculated values for two orientations. The isoenergy contours in Figure 2 have been obtained from the potential function by fixing the water oxygen and then optimizing the orientation in order to obtain the minimum energy. The two contour maps, one with the benzene molecule in the plane and one perpendicular to the plane, indicate that there is only one

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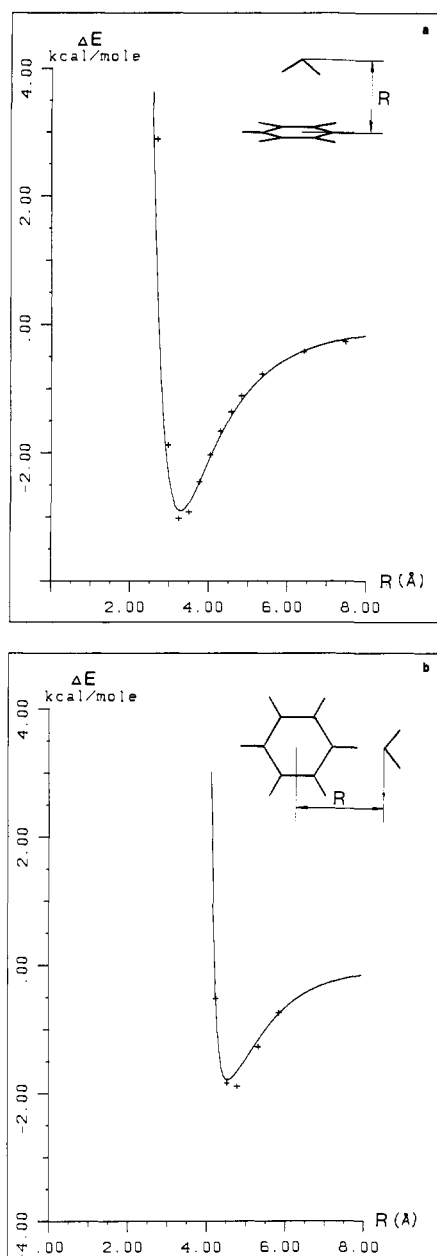


Figure 1. Potential energy curves of benzene and water along two directions with fixed orientations. (a) The symmetry axes of the two molecules coincide, and the water hydrogens are located in the x,z plane and point toward the benzene molecule. (b) Both molecules are in the same plane, the water symmetry axis coincides with one C_2 axis of benzene going through two hydrogen atoms, and the water hydrogens point away from the benzene molecule. The plus signs are *ab initio* calculated energies, ΔE_{01} , and the solid lines are fitted energy curves.

symmetry-independent local minimum in the intermolecular potential. In the global minimum shown in Figure 2b, the water molecule is tilted slightly away from the benzene symmetry axis. The interaction energy for this geometry is -2.99 kcal/mol from the potential function and -3.15 kcal/mol from calculations, respectively.

The benzene–benzene potential function was based on 72 points, and ϵ was 0.24 kcal/mol here also. In Figure 3, four different cuts in the intermolecular potential hypersurface for benzene–benzene are presented together with quantum mechanically calculated points. For two of the cuts, we have included points representing the empirical potential of Evans and Watts.^{35,36} It

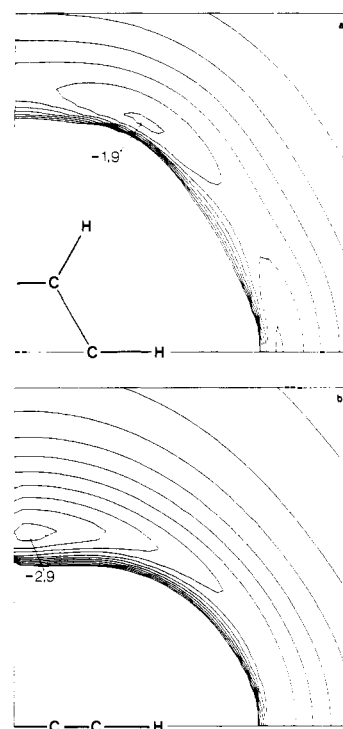


Figure 2. Energy contour maps for the water–benzene interaction with fixed oxygen position and optimized water orientations. The benzene molecule is held fixed in the x,y plane, and the symmetry axis coincides with the z -axis. In a, the oxygen atom is in the x,y plane, and in b, it is in the x,z plane. Contour distance is 0.3 kcal/mol.

can be seen that the two potentials describe the lowest minimum in a similar way but that the empirical potential predicts geometry 1 to be more stable than our quantum chemical potential. In their discussion, Watts and Evans argue, however, that their potential probably is too binding for this orientation. Figure 4 shows isoenergy contours, which are obtained by fixing one benzene molecule at the origin, fixing the mass center of the other benzene molecule, and optimizing its orientation to obtain the minimum energy.

The potential functions obtained have also been used to calculate the second cross virial coefficient for water and benzene and the second virial function for benzene (Figure 5). Unfortunately, there does not seem to be any experimental data for the cross virial coefficient for water and benzene. Included in Figure 5 are also the experimental virial coefficients for pure benzene and pure water. It can be seen that the calculated virial coefficient is approximately 25% too negative. If we assume that the most important contributions to the virial coefficient come from the attractive parts of the potential, we can make a crude estimate of the error in the potential by equating $\ln 1.25 = \Delta\epsilon/RT$, giving an average error $\Delta\epsilon \approx 0.1$ kcal/mol in the potential—a satisfactory result.

It has been shown in this work that MB SCF calculations (MB = minimal basis) are not capable of predicting intermolecular potentials unless one corrects for the superposition error, the errors in electrostatic and induction interactions, and the lack of dispersion interaction in the SCF calculations. This is consistent with the results in a recent work, where it was found possible to reproduce the results of large basis SCF calculations for the N_2 dimer with minimal basis calculations provided that the necessary corrections were performed.¹⁸ The use of MB SCF technique for calculating intermolecular potentials is then only justified by computational simplicity, but since the amount of computer time needed to perform the suggested corrections amounts to only a

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Table III. Partitioning of the Total Interaction Energies for the Water-Benzene System^a

| R | ΔE^*_{SCF} | E_{BSSE} | $E_{\text{es}} - E^*_{\text{es}}$ | $E_{\text{ind}} - E^*_{\text{ind}}$ | E_{disp} | ΔE_{tot} |
|----------------|---------------------------|-------------------|-----------------------------------|-------------------------------------|-------------------|-------------------------|
| Orientation I | | | | | | |
| 2.68 | 6.57 | 3.6 | -1.1 | 0.0 | -6.14 | 2.87 |
| 2.95 | 0.92 | 1.7 | -0.5 | -0.1 | -4.00 | -1.90 |
| 3.21 | -1.01 | 0.8 | -0.2 | -0.1 | -2.62 | -3.04 |
| 3.74 | -1.45 | 0.2 | 0.0 | 0.0 | -1.16 | -2.47 |
| 4.27 | -1.09 | 0.0 | 0.0 | -0.0 | -0.54 | -1.67 |
| 6.39 | -0.40 | 0.0 | 0.0 | 0.0 | -0.05 | -0.44 |
| Orientation II | | | | | | |
| 3.97 | 10.53 | 2.5 | 0.8 | -4.9 | -3.66 | -5.26 |
| 4.23 | 1.20 | 2.0 | 0.4 | -1.7 | -2.38 | -0.54 |
| 4.50 | -1.22 | 1.5 | 0.2 | -0.7 | -1.58 | -1.87 |
| 4.76 | -1.50 | 0.9 | 0.1 | -0.3 | -1.04 | -1.90 |
| 5.29 | -1.01 | 0.2 | 0.0 | -0.1 | -0.43 | -1.29 |
| 5.82 | -0.59 | 0.1 | 0.0 | 0.0 | -0.19 | -0.76 |

^a See eq 4 and 9. The two orientations are described in the text. Units are kilocalories per mole and angstroms.

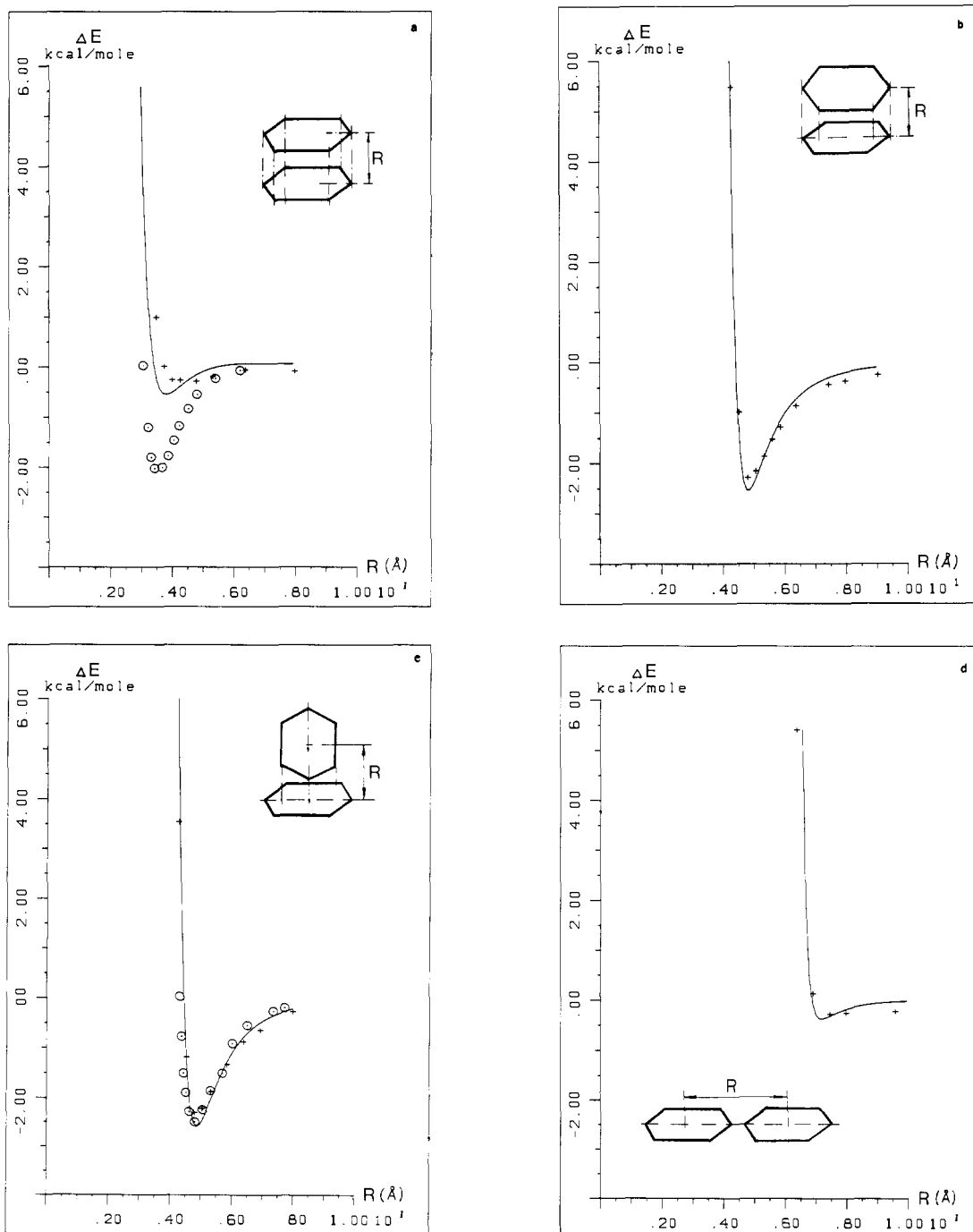


Figure 3. Potential energy curves of the benzene dimer for four different orientations (the orientations are shown in the inserts): (+) *ab initio* calculations points; (—) fitted curves; (⊙) from the empirical benzene-benzene potential of Evans and Watts.^{35,36}

Table IV. Coefficients of the Water-Benzene Potential Function^a

| <i>i</i> | <i>A_i</i> | <i>B_i</i> | <i>C_i</i> | <i>D_i</i> | <i>E_i</i> |
|----------|----------------------|----------------------|----------------------|----------------------|----------------------|
| C-O | 33.658 | 163.883 | -2586.96 | 44883.5 | 109 937 |
| C-H | -16.829 | -94.375 | 858.81 | -6506.8 | 27 667 |
| H-O | -33.658 | -176.163 | 1144.37 | -5840.7 | 13 935 |
| H-H | 16.829 | 100.514 | -642.56 | 2238.8 | 3 119.7 |

^a Units are in kilocalories per mole and angstroms.

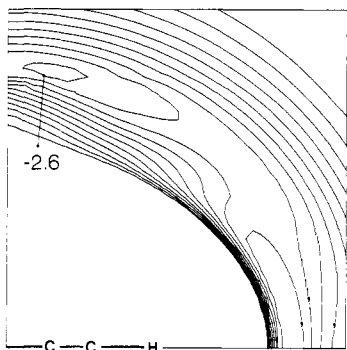


Figure 4. Energy contour map for the benzene-benzene system. The symmetry axis of the benzene molecule at the origin coincides with the *z* axis. The mass center of the second benzene molecule is fixed in the *x,z* plane, and its orientation is optimized. Contour distance is 0.2 kcal/mol.

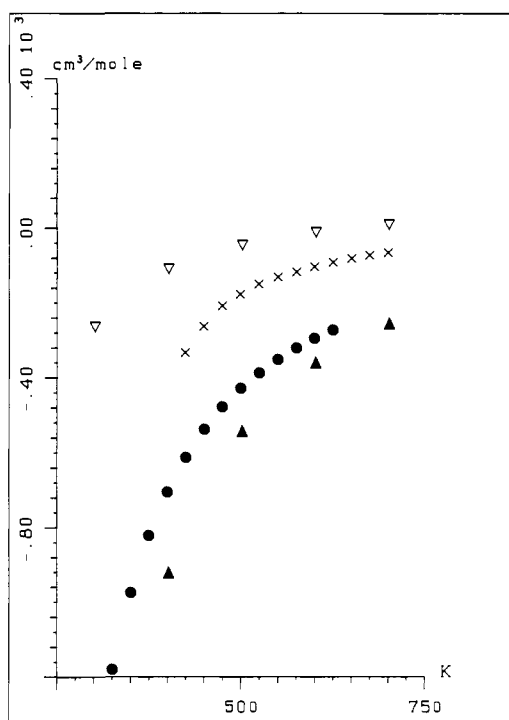


Figure 5. Second virial coefficient for (▽) water-benzene (this work), (▲) benzene-benzene (this work), (×) water-water,³⁹ (●) benzene-benzene.⁴⁰

small fraction of the time for the MB SCF calculation, this argument also seems less appropriate.

The idea of partitioning the total interaction energy into contributions with physical meaning makes it clear that each of these contributions must be carefully described in order to obtain reliable

Table V. Coefficients of the Benzene-Benzene Potential Function^a

| <i>i</i> | <i>A_i</i> | <i>B_i</i> | <i>C_i</i> | <i>D_i</i> | <i>E_i</i> |
|----------|----------------------|----------------------|----------------------|----------------------|----------------------|
| C-C | 7.3365 | -29.468 | -325.44 | 16005.8 | 194 320 |
| C-H | -7.3365 | 27.889 | -286.60 | 1641.5 | 27 667 |
| H-H | 7.3365 | -26.310 | 114.73 | -590.0 | 3 119.7 |

^a Units are in kilocalories per mole and angstroms.

interaction energies. In order to judge whether the proposed scheme meets these requirements, the method must be further tested on several systems where comparison with more experimental data is possible. One may, however, conclude from the tests made so far that this method seems far more promising than standard MB SCF calculations for the construction of intermolecular potentials.

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Appendix 1

As mentioned above, the extension of the model for the evaluation of the interaction energy from a minimal to an extended basis set is not straightforward. Due to the diffuse character of some of the virtual orbitals, the localization process resulted in orbitals with a center of charge almost 1 Å outside the hydrogen atoms in the benzene molecule. Consequently, for some geometries, the overlap between the two interacting charge distributions turned out to be very large, and the multipole expansion of the integral in the numerator broke down. Instead, the charge distribution ($\phi_i(1) \rightarrow \phi_j(1)$) for the excitation from orbital $\phi_i(1)$ to orbital $\phi_j(1)$, where index 1 stands for molecule A, was represented by

$$f_{ij}(x,y,z)e^{\alpha_{ij}(r-\bar{r}_{ij})^2}$$

where $\bar{r}_{ij} = 1/2(\bar{r}_i + \bar{r}_j)$ and \bar{r}_i is the center of the charge for an electron in orbital ϕ_i . To estimate α_{ij} , the expectation value of r^2 was calculated for each orbital

$$\langle r^2 \rangle_i = \int \phi_i(\bar{r} - \bar{r}_i)^2 \phi_i d\tau$$

If the orbital ϕ_i is assumed to be a Gaussian charge distribution centered at r_i , the calculated expectation value could be related to an average exponent α_i for orbital ϕ_i according to

$$\alpha_s = -3/(4\langle r^2 \rangle) \quad (\text{A1})$$

$$\alpha_p = -5/(4\langle r^2 \rangle) \quad (\text{A2})$$

where eq A1 is valid if the orbital ϕ_i is represented by an s function centered at r_i and eq A2 if it is mimicked by a p basis function having the same origin. In this work, an average of eq A1 and A2 has been used: $\alpha_i = -\langle r^2 \rangle^{-1}$. α_{ij} is then taken as the sum of α_i and α_j . The functions $f(x,y,z)$ have been chosen in order to obtain the dipole and quadrupole moments for the charge distribution resulting from the orbital product $\phi_i\phi_j$. To make the procedure unique, it has been assumed that all higher order moments should be zero.

The numerator in eq 8 above has then been evaluated by substituting the orbital products $\phi_i(1)\phi_j(1)$ by $f_{ij}(x,y,z)e^{\alpha_{ij}(r-\bar{r}_{ij})^2}$. This means that the procedure used is equivalent to the one previously used²⁶ when the orbital exponent α_{ij} is infinite, i.e., overlap is neglected.

Registry No. Water, 7732-18-5; benzene, 71-43-2.